

Supporting Information

Solvent controlled sugar-rhodamine fluorescence sensor for Cu²⁺ detection

Xing Ma ^{a,b}, Zhuowei Tan ^a, Guohua Wei ^{a,*}, Dongbin Wei ^{a,*}, Yuguo Du ^{a,b,*}

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

^b College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding authors: Guohua Wei, E-mail: wgh@rcees.ac.cn; Dongbin Wei, E-mail: weidb@rcees.ac.cn; Yuguo Du, E-mail: duyuguo@rcees.ac.cn

Materials and Measurements

Fluorescence spectra were obtained by using a Hitachi F-7000 Fluorescence Spectrometer equipped with a xenon lamp, 1.0 cm quartz cell, and slits of 1.0/1.0 nm. All chemicals were of reagent grade and used without further purification. Ultrapure water with a Millipore Purification System (Milli-Q water) was used throughout the analytical experiments. The ¹H and ¹³C NMR spectra were recorded on ARX 400 spectrometers for solutions in CDCl₃. Chemical shifts are given in ppm downfield from internal Me₄Si. Mass spectrometry was conducted in a positive mode using MALDI-source. Thin layer chromatography (TLC) was performed on silica gel HF₂₅₄ with detection by charring with 30% (v/v) H₂SO₄ in MeOH or in some cases by a UV detector.

NMR data of probe 1

¹H NMR (CDCl₃, 400 MHz) δ (TMS, ppm): 1.31-1.34 (m, 6H), 1.89-1.92 (m, 6H), 2.75-2.95 (m, 2H), 3.09-3.14 (m, 2H), 3.18-3.23 (m, 5H), 3.38-3.40 (m, 1H), 3.45-3.75 (m, 5H), 4.36 (d, *J* = 3.2 Hz, 1H), 5.65 (s, 1H), 6.12 (s, 1H), 6.19 (s, 1H), 6.34 (s, 1H), 6.37 (s, 1H), 7.04 (dd, *J* = 1.6, 6.4 Hz, 1H), 7.47-7.51 (m, 2H), 7.93 (dd, *J* = 1.6, 6.4

Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (TMS, ppm): 14.72 (2C), 16.72, 16.76, 38.32, 38.39, 62.33, 65.56, 67.60, 70.46, 70.82, 90.13, 96.14, 96.93, 103.36, 105.89, 117.66, 118.21, 123.26, 124.42, 127.59, 128.31, 128.43, 128.88, 133.71, 147.57, 147.81, 151.89, 152.60, 152.70, 170.29.

Sample preparation

The stock solutions of probe **1** (1.0 mM) and Cu^{2+} (1.0 mM) were prepared in pure water containing 20% of acetonitrile, and their corresponding working solutions were simply prepared by diluting with water containing 20% of acetonitrile.

Fluorescence analysis

A 0.10 mL of probe **1** (1.0 mM) solution (containing 20% of acetonitrile) was blended with 0.1 mL of Cu^{2+} solution (containing 20% of acetonitrile) in a 10 mL colorimetric tube. The mixture was equilibrated for 30 min and then the fluorescence intensity was recorded at $\lambda_{\text{ex}}/\lambda_{\text{em}} = 520/560$ nm alongside a reagent blank. The excitation and emission slits were both set to 1.0 nm.

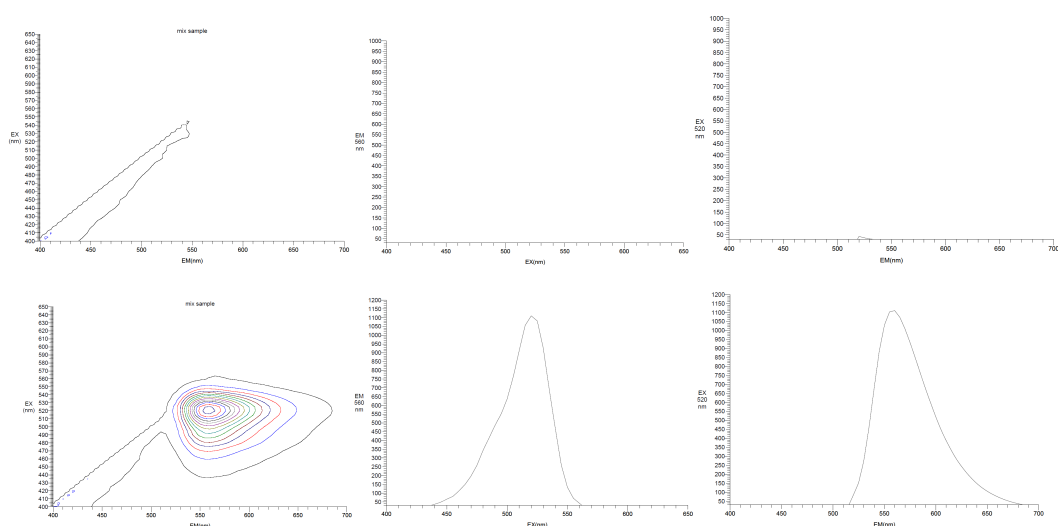


Fig. S1. The three-dimension excitation emission matrix fluorescence spectroscopy (3D-EEM) of probe **1** (10 μM) without and with presence of 10 μM Cu^{2+} .

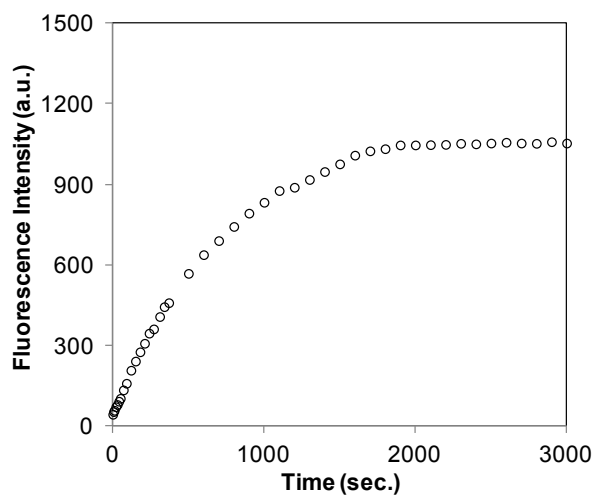


Fig. S2. The change of fluorescence intensity ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 520/560$ nm) of probe **1** (10 μM) with time in the presence of 10 μM of Cu^{2+} in water containing 20% CH_3CN at room temperature.

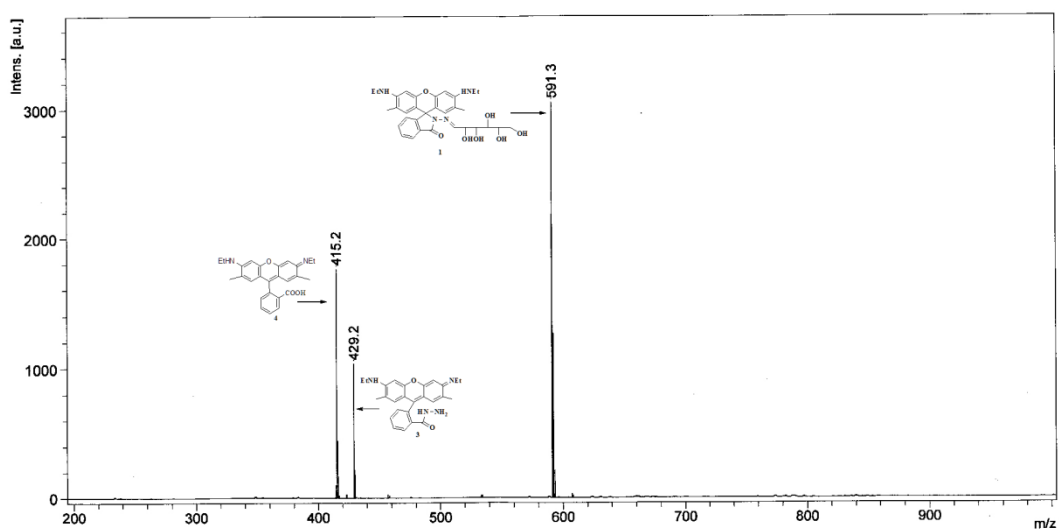


Fig. S3. MALDI-TOF-Mass spectrum of the raw solution (namely, probe **1** + Cu^{2+}) in a short 5 min reaction time.

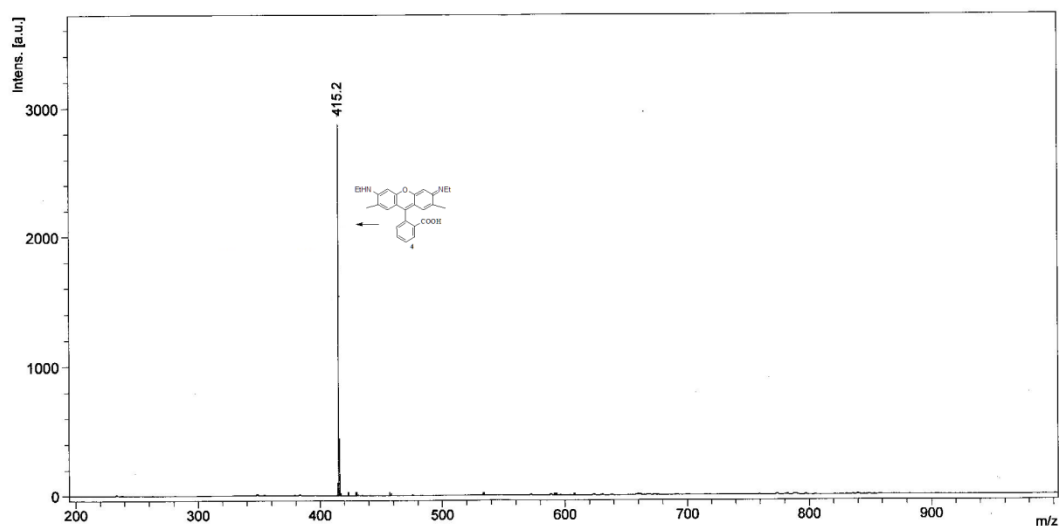


Fig. S4. MALDI-TOF-Mass spectrum of the raw solution (namely, probe **1** + Cu^{2+}) in a long 30 min reaction time.

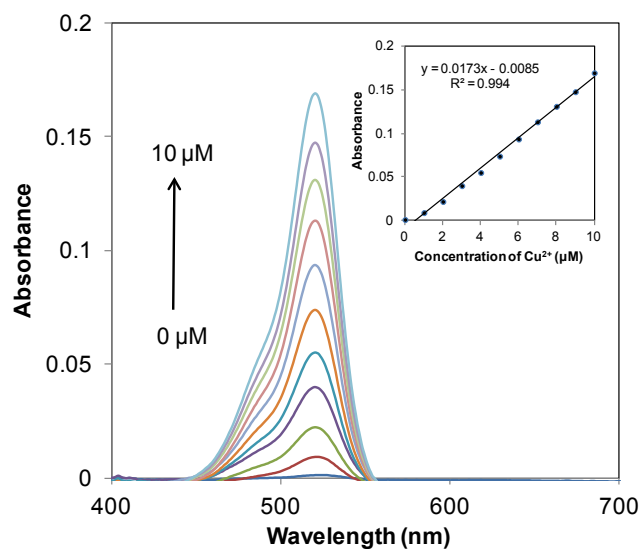


Fig. S5. UV-Vis absorption titration spectra of probe **1** (10 μM) with Cu^{2+} from 0 to 10 μM in water containing 20% (v/v) of CH_3CN . Inset: The plot of UV-Vis absorbance change of probe **1** (10 μM) against varied concentration of Cu^{2+} from 0 to 10 μM at $\lambda = 520 \text{ nm}$.